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A Dielectric Relaxometry Study of Segmental Dynamics in PDMS/Boron Composite and Hybrid Elastomers

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ABSTRACT

In this work, the motional dynamics and relaxation behavior of a series of model Poly(dimethylsiloxane)-*co-m*Carborane (PDMS-*co*-CB) hybrid elastomers have been studied in depth, using Broadband Dielectric Spectrometry over a temperature range of -130 to 100 °C and a frequency window of 10^{-1} to 10^7 Hz. The segmental α -relaxation of both the PDMS and Carborane chain segments have been characterized at specific Carborane backbone incorporation levels with a direct correlation between the ratio of PDMS to Carborane segments and the motional constraint of the network as a whole was observed. In addition to the study of the α -motional modes associated with local intra-segmental motions and the onset of cooperative motion, we have also identified and studied a higher order cooperative (normal-mode) motion of extended segments of the Carborane-siloxane co-polymer chains at elevated temperatures. These normal mode motions have been shown to follow an Arrhenius temperature dependence, are sensitive to the local chemical environment and have not been previously

reported in this class of polysiloxane copolymer. The motional dynamics of the PDMS-*co*-CB networks have been compared and contrasted with those of a series of conventionally filled PDMS-Boron Nitride (PDMS-BN) composite systems. While the effects of the chemically bound Carborane segment on the PDMS chain dynamics, local order and global network properties have been shown to be directly correlated, significant and predictable, the effects of the BN filler on the PDMS matrix is significantly less so and the results suggest that the filler material may in-fact be disrupting the network order, with a consequently negative impact on the properties of the composite.

KEYWORDS

Poly(dimethylsiloxane); *m*Carborane ; Dielectric Relaxometry; Segmental Dynamics; Nanocomposites; Nanohybrids

INTRODUCTION

Crosslinked polysiloxane elastomeric networks are an academically and technologically relevant class of inorganic polymeric system and over the last 50 years, these materials have found wide-spread application in a number of diverse technological, commercial and research areas[1-4]. Simple end-linked, unfilled, condensation, addition or peroxy- cured PDMS networks typically exhibit poor mechanical properties and are of limited use as practical materials[5]. It is understood that in order to obtain the desired combinations of mechanical, physical and chemical properties for a specific real world application, polysiloxane materials must be formulated as complex multi-component systems - incorporating multi-modal distributions of chain lengths, varied crosslink topologies/densities, chemically modified free chain ends, non-stoichiometric excesses of reactive moieties, and often large volume fractions of a variety of reactive and/or passive filler materials.

Fillers are of particular importance as physical property modifiers in polysiloxane systems and are typically, micron or nano-scale inorganic materials (fumed silica, amorphous carbon, aluminosilicate clay) that are introduced into the polymer matrix as a heterogeneous 2nd phase to form a composite with

improved physical properties. Both the requirement for and the mechanisms of reinforcement in such polysiloxane composites were established thoroughly in the 1970s by both Wager [6] and Boonstra [7-9].

Today, these approaches to physical property modification are well established and are the mainstay of industry and technologists - who seek to formulate practical polysiloxane based elastomer systems for application. However, with new applications [3, 10, 11] come ever increasing demands for new classes of polysiloxane materials with improved, better defined and even novel materials properties. As a result of these drivers, there has been a corresponding increase in research devoted to the physical and chemical incorporation of nano-scale fillers and additives into polysiloxane systems [12-14]. The goal of these efforts has been to achieve both large and predictable improvements in materials properties at low mass fractions of the nano-material additive. This *nano-modification* of polysiloxane systems has met with mixed success over the last 20 years and can be broadly be separated into two main classes; the formation of nanocomposites through the physical blending of a nano-scale 2nd phase into a polymeric system, and the synthesis of nano-hybrid materials – where a well-defined nano-scale inorganic structure such as a cage is chemically bound into the polymer network to form a hybrid material. Both approaches are quite different and have their advantages and disadvantages: The physical incorporation of a nano-scale 2nd phase into polysiloxane systems have been shown to be both beneficial [12, 15, 16] and deleterious [17-19] to the properties of the final composite. It is clear that the inclusion of nano-scale materials into a polysiloxane matrix often has unpredictable effects on materials properties [18, 20] and the mechanisms of property modification remain poorly understood. The polysiloxane-nanohybrid materials route potentially offers improved control and predictability of materials properties [15, 18]. However, the controlled synthesis of these materials can be complex [21] and subject to the limitations of the coupling chemistries available [5, 22]. Additionally, the covalent inclusion of the nano-material alters the chemical properties of the polysiloxane matrix to the extent that those properties which make PDMS and its relatives attractive [1, 2, 23] are diluted or lost in the final material.

The current state of the art is that there are now a number of materials, systems and strategies available for both the physical and chemical nano-modification of polysiloxanes, but the understanding of the mechanisms of physical reinforcement in particular, are not fully understood [24]. What is accepted however is that it is the polymer segmental dynamics, the local ordering dynamic free volume and the perturbation/modification of these behaviors over a range of size and timescales which ultimately define the properties and performance of a nanocomposite or nanohybrid system [25, 26].

Characterizing the motional dynamics and order in polysiloxane composite and hybrid systems can provide key insight into structure-property relationships and the mechanisms of physical property modification. And indeed, the authors and others have previously used a range of techniques to probe polymer segmental dynamics in relation to nano-materials inclusion and incorporation in a range of polymer systems: Saalwacher *et al.* made use of low field nuclear magnetic resonance (NMR) methodologies to study the effects of functionalized silica nano-particles on the chain dynamics of polyester amide blends [27]. Lewicki *et al.* have employed high field multiple quantum (MQ) NMR in combination with broadband dielectric spectroscopy (BDS) to probe the effects of physically incorporated *o*-Carborane cages on the segmental dynamics of a crosslinked poly(dimethylsiloxane) (PDMS) elastomer [20]. More recently, Alam *et al.* have studied the effects of Carborane and polyhedral oligomeric silsequioxane (POSS) moieties on the global free volume of model PDMS elastomers through the use of positron annihilation lifetime spectroscopy (PALS) [28]. These studies and others like them, serve to underline the fact that while the effects of nano-materials incorporation and inclusion into polysiloxane materials are often unexpected, by studying the physical polymer chain dynamics of a system, the influence of nano-scale property modifiers may be predicted and even successfully tailored to application.

In this work, the motional dynamics and relaxation behavior of a series of model PDMS/PDMS-co-*m*Carborane (PDMS-co-CB) hybrid elastomers have been studied in depth using BDS over a broad range of temperatures. The segmental α -relaxation of both the PDMS and Carborane chain segments have been characterized in full over a range of Carborane backbone incorporation levels. Additionally,

the higher order cooperative (normal-mode) motions of extended Carborane-siloxane segments have been characterized at elevated temperatures. These data have been compared to a series of conventionally filled PDMS-Boron Nitride (PDMS-BN) composite systems and the effects of the chemically bound Carborane segment on the PDMS chain dynamics, local order and global properties of the systems are directly contrasted that of the PDMS-BN composites.

EXPERIMENTAL

Materials. Hydroxyl terminated poly(dimethylsiloxane) (PDMS) resin ($M_n = 26,000 \text{ g.mol}^{-1}$, Gelest DMS-S31), tin(II) 2-ethylhexanoate (Sigma-Aldrich, 95%), tetraethoxysilane (TEOS, 98%, Sigma-Aldrich,) and boron nitride powder (hexagonal, sub- μm particle size, 99%, Sigma-Aldrich) were purchased from their respective supplier and used without further purification. Linear and regular poly(carborane-*co*-siloxane) was prepared at AWE *via* a novel route.

Materials Synthesis and Preparation. The desired amounts of hydroxyl-terminated poly(dimethylsiloxane) resin, poly(carborane-*co*-siloxane), BN powder and TEOS were shear mixed using a Hauschald DAC 150 FVZ-K speedmixer. The formulation was allowed to cool to room temperature before addition of tin(II) 2-ethylhexanoate to catalyse cross-linking. The mixture was then moulded under pressure at room temperature to produce 2 mm thick flat sheets. The resulting pads were post-cured at 75 °C in air. Given in **Table 1** is a summary of the hybrid and composite systems formulated for this study.

Table 1. Summary of BN filled and hybrid PDMS-*co*-*m*CB materials formulated

Sample Code	BN loading (wt%)	Carborane (wt.%)	PDMS to (co- <i>m</i> CB) ratio (mass)	co- <i>m</i> CB (wt.%)
Base	0	0	1:0	0
FSL	19.99	0	1:0	0
FSM	30.68	0	1:0	0
FSH	40.50	0	1:0	0
FSvH	49.80	0	1:0	0
DvL	0	2.89	10.5 : 1	8.7
DL	0	6.67	4:01	20

DM	0	10.13	2.3 : 1	30.3
DH	0	21.82	0.54 :1	64.9

Dielectric Relaxometry Analysis. All BDS analyses were carried out using a Novocontrol Concept 40 Dielectric Spectrometer system based upon an Alpha-A combined frequency response analyzer/signal generator/charge amplifier assembly and a Quatro cryostat sample temperature control system. The instrument had a working frequency range of 10^{-5} to 10^7 Hz and a stable sample temperature range of -160 to 300°C. All BDS analyses reported in this paper were carried out using a computer controlled frequency domain method as described by D. Hayward *et al.* [29]. Samples of ~2 mm thickness and 20 mm in diameter were analyzed under a constant flow of N₂ in a parallel plate configuration cell with an upper electrode diameter of 10 mm.

PDMS has a net dipole moment as a result of the polar Si-O bond and the asymmetry of the chain backbone. It is possible therefore to resolve the α -segmental relaxation for PDMS chains. This relaxation is typically observed at ~500 Hz at -125 °C; however it is necessary to quench the polymer to a temperature significantly below T_m (-55°C for pure PDMS) so as to prevent crystallization of the sample and inhibition of the α -process. Experimentally, this was achieved by assembling the sample/electrode sandwich and immersing is in LN₂ for 1 minute before transferring the now quenched sample to the cryostat and allowing it to equilibrate to a temperature of -140°C for 30 minutes, before commencing the analysis. Normal mode relaxations (large scale, multi-segment cooperative chain motions) generally observed at temperatures well above the T_g of PDMS (-123 °C) and therefore require no quenching treatment prior to analysis.

Data were recorded as the real and imaginary components of the complex dielectric permittivity (ϵ) as a function of frequency and temperature. These data were further processed by an empirical minimization routine which fitted one or more Havriliak-Negami (H-N) dispersion curves and a linear dc conductivity component to the complex dataset, as described in **Equation 1**.

$$\varepsilon(\omega) = \varepsilon' - i\varepsilon'' = -i \left(\frac{\sigma_0}{\varepsilon_0 \omega} \right)^N + \sum_{k=1}^3 \left[\frac{\Delta\varepsilon_k}{(1 + (i\omega\tau_k)^{\alpha_k})^{\beta_k}} + \varepsilon_{\infty k} \right]$$

Where ω is the angular frequency, ε' and ε'' are the real and imaginary components of the complex permittivity respectively, σ is the conductivity in $S\ cm^{-1}$, ε_0 is the vacuum permittivity ($8.854 \times 10^{-12}\ F\ m^{-1}$). α and β Are the pre- and post-exponential factors which correspond the curve width and asymmetry parameters respectively. For a simple Debye process α and $\beta = 1$. N is the exponential factor for the conductivity term and it determines the slope of the conductivity component.

The fitting program utilized a Levenberg-Marquardt minimization routine to arrive at parameters which fit one or more H-N dispersion curves and a linear conductivity component to the experimental data. Experimentally it has been found that minimizing on the modulus of the complex permittivity gives the most stable solutions [30].

RESULTS AND DISCUSSION

The PDMS α -relaxation as a probe of chain and network dynamics. For both the filled PDMS and the PDMS/PDMS-*co*-*m*CB hybrid networks, the α rotation of the $[Si(Me)_2O]$ segment can be observed. This primary segmental rotation is associated with the onset of cooperative motion and the glass to rubber transition (T_g) of PDMS. As such, the segmental α -relaxation is both sensitive to changes in both the local chain environment and the global network structure. In the unfilled PDMS elastomer, the unconstrained α -relaxation was observed over a temperature range of -125-105 °C (see **Figure 1**).

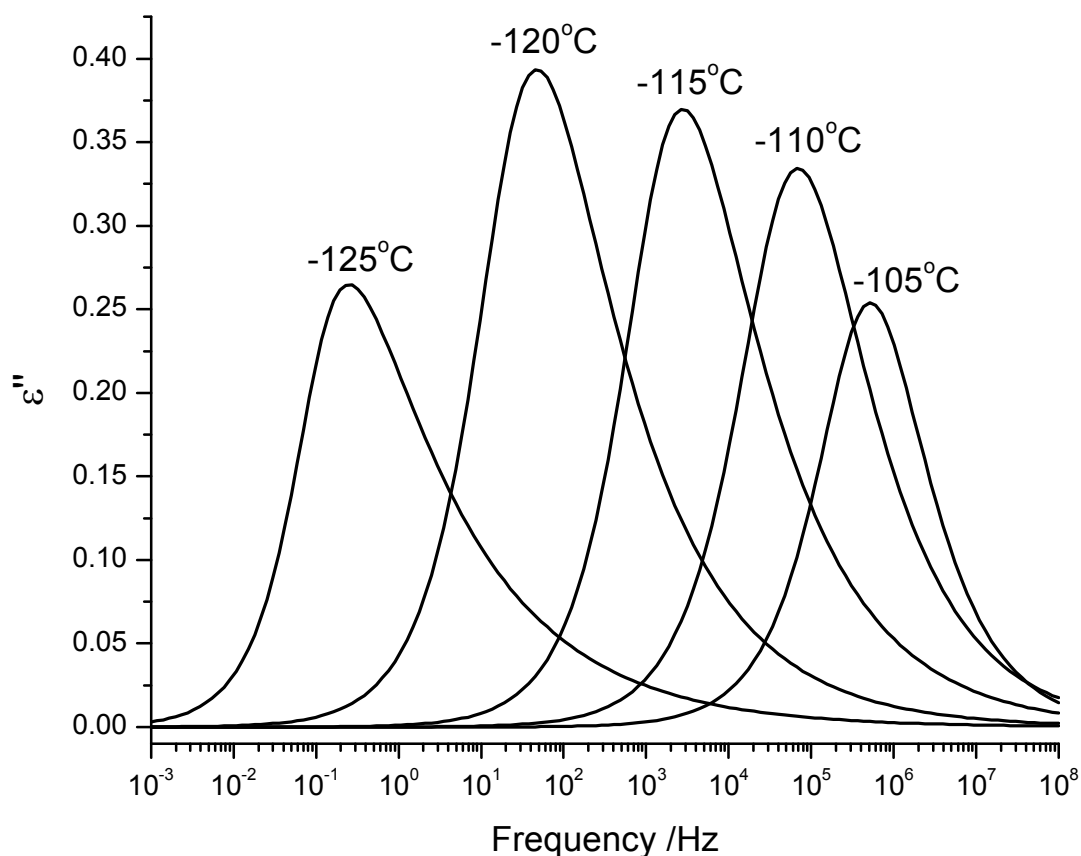


Figure 1. The resolved α segmental relaxation of PDMS in the unfilled, base PDMS network. Note that the relatively low activation barrier for segmental chain motion in PDMS results in several orders of magnitude increases in the rate of chain motion for correspondingly small increases in temperature.

At temperatures above $-100\text{ }^{\circ}\text{C}$, a secondary α_c -relaxation manifested as a result of the rapid cold-crystallization of the now mobile PDMS segments above the T_g of the system. PDMS can become up to 95% crystalline by weight and this constrained α -motion originates from the relaxation of amorphous PDMS domains that lie between crystalline lamellae in a predominantly crystalline system. Shown in **Figure 2** is a comparison of the unconstrained and constrained α and α_c relaxations in the unfilled PDMS elastomer.

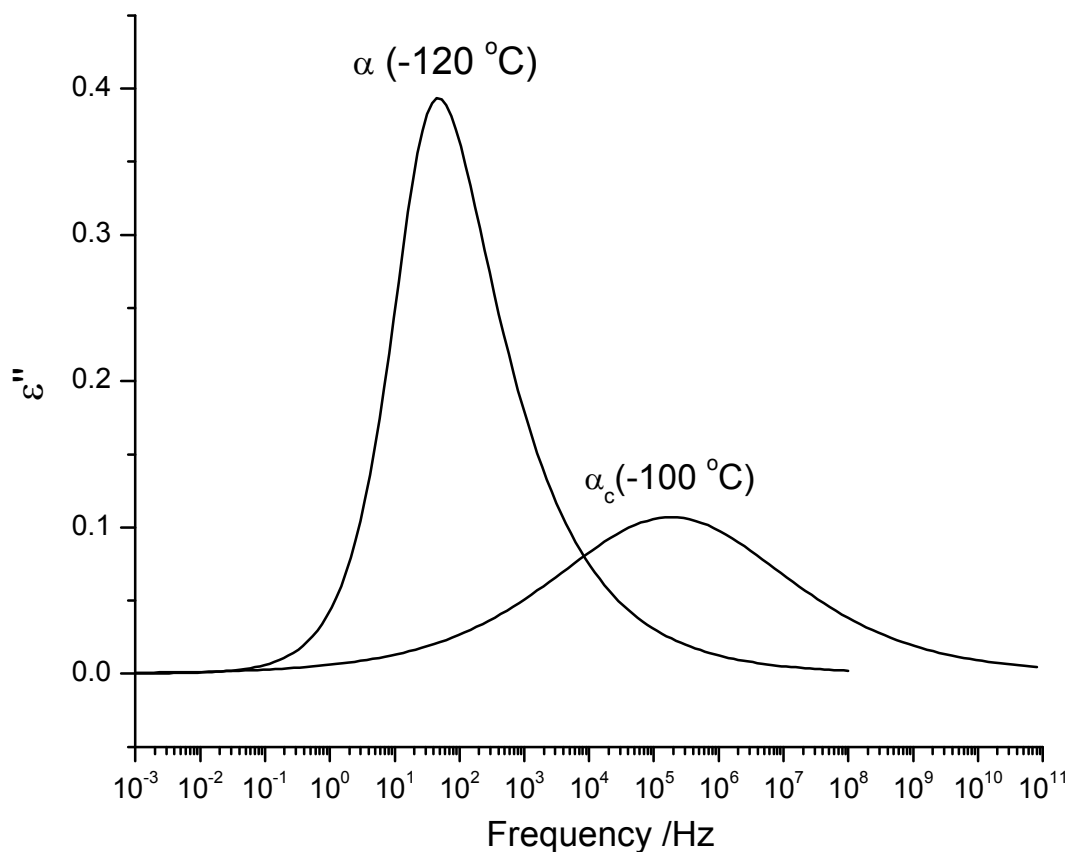


Figure 2. A comparison between the α -relaxation in the unfilled PDMS elastomer and the highly constrained α_c -relaxation which results from the rapid cold-crystallization of the PDMS chains at temperatures above ~ -123 °C (the T_g). Note that due to the comparative immobilization of the remaining amorphous PDMS segments between rigid crystalline lamellae, the α_c deviates significantly from a simple Debye process and the relaxation is broadened significantly.

For the purposes of this study, it is the motion of amorphous PDMS chains in relation to both the BN filler and the *co-mCB* chain segments that are of interest, therefore the α_c -relaxations will be largely ignored. However the data in **Figure 2** does serve to illustrate clearly the sensitivity of the α -relaxation to its local motional environment in PDMS systems.

In order to investigate the effects of both BN filler particle inclusion and PDMS-*co-mCB* polymer incorporation on the motional dynamics of the PDMS matrix, the α -relaxations of each material have been compared at -120°C . Given in **Figure 3** are the resolved PDMS α -relaxations for the filled and hybrid systems. **Figure 4** summarizes the trends in the characteristic relaxation time (τ), which is a

measure of the comparative ease of the rotational chain segmental motion which is coupled with each resolved relaxation (where ω is the frequency of the resolved relaxation).

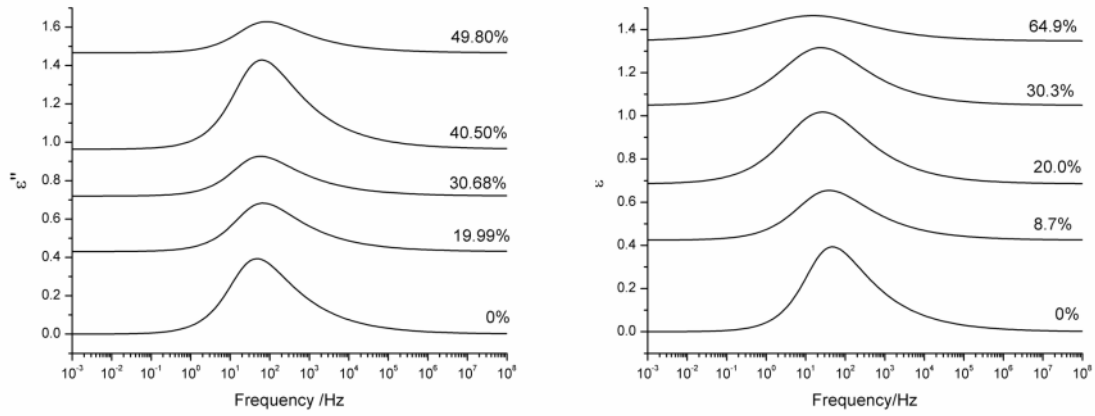


Figure 3. Resolved PDMS α -relaxations at -120°C for the BN filled PDMS elastomers (left) and PDMS/PDMS-co-*m*CB hybrid elastomers (right) as a function of wt. % BN and co-*m*CB respectively. For the BN filled systems we observe no trend however the PDMS/PDMS-co-*m*CB materials show a clear trend of decreasing amplitude of the α -relaxation and a shift towards lower frequencies as a function of increasing wt. % co-*m*CB.

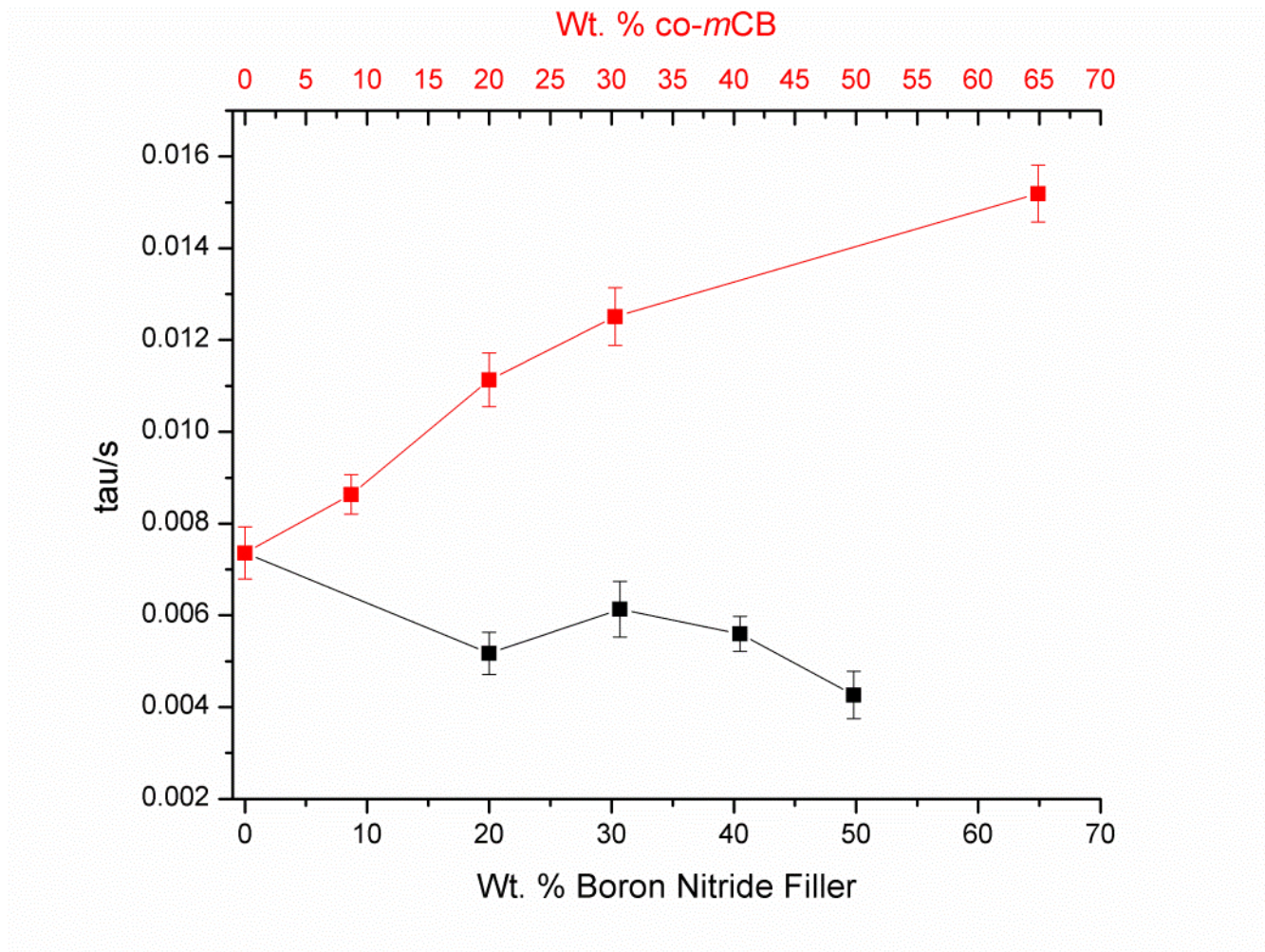


Figure 4. Trends in the characteristic relaxation time, τ at -120°C for the BN filled PDMS elastomers (black) and the PDMS/co-*m*CB hybrid elastomers (red). Note that τ increases significantly as a function of co-*m*CB polymer content (from ~7 to 16 ms at the highest co-*m*CB level) - which is indicative of a significant reduction in PDMS segmental mobility, whereas τ actually decreases slightly in as a function of BN loading.

The analysis of the PDMS segmental α -relaxations, given in **Figures 3&4** clearly show that the covalent inclusion of an PDMS-co-*m*Carborane polymer into the PDMS network has a significant and global effect on the motional dynamics of the system. The *m*CB co-polymer segments are reducing the mobility of the PDMS chains and effectively stiffening the network in a predictable and controlled manner. The simple physical addition of BN particles shows no such predictability or control and in fact, the relaxation time data shows that the PDMS segmental mobility increases as a function of BN loading. This decrease in τ suggests that the BN filler is disrupting the network order - either chemically

(through a reduction in effective cross-link density/topology) or physically through network plasticization.

Analysis of the co-*m*CB segmental α -relaxation. The PDMS/PDMS-*co-m*CB hybrid elastomers exhibit a distinct 2nd relaxation, observed between -65 and -35°C which has been attributed to the segmental α -relaxation of the *co-m*CB polymer chains. The activation barrier for this segmental motion is significantly higher, owing to the large steric penalty acquired through the rotation of complete Carborane cage vs. a single [Si(Me)₂O] segment. In **Figure 5**, the resolved *m*CB segmental α -relaxation is given as a function of co-*m*CB level.

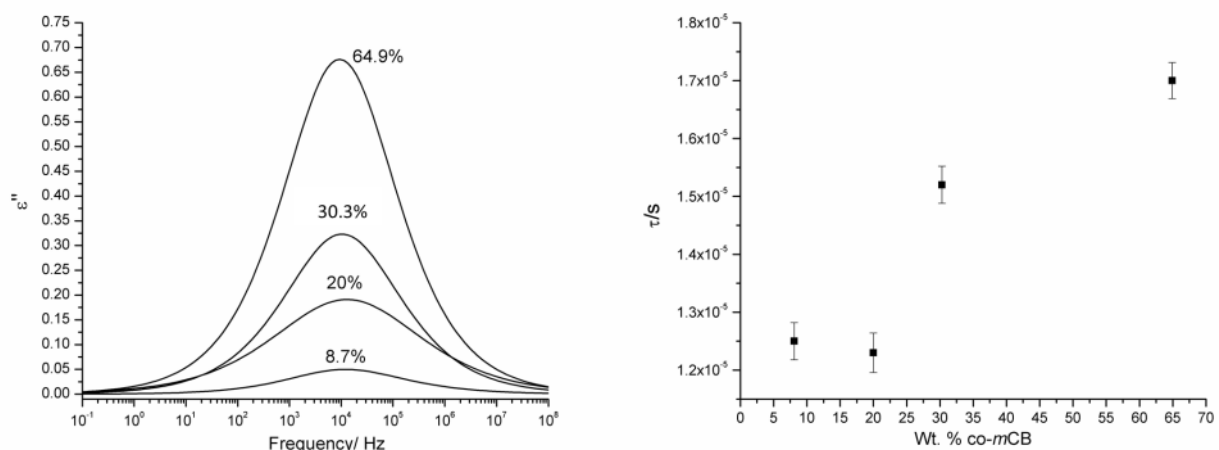


Figure 5. *Left:* The *m*CB segmental α -relaxation at -50°C as a function of wt. % *co-m*CB in the hybrid PDMS elastomers. Note that amplitude of the relaxation increases in proportion with the levels of *co-m*CB in the elastomer. *Right:* the relaxation time for the segmental motion at -50 °C as a function of *co-m*CB incorporation level. There is a small but real increase in τ as the % of *m*CB is increased in the hybrid systems.

From the analysis of the *m*CB α -relaxation given in **Figure 5** it is apparent this motional mode is both distinct from the PDMS α -relaxation and the intensity of this process clearly increases as a function of the co-*m*Carborane loading in the hybrids. The small increase in τ as a function of *m*CB incorporation level is again attributed to a global reduction in chain mobility within the hybrid networks. However it is also noteworthy that this higher activation barrier segmental process appears less sensitive to its local motional environment than that of the highly mobile PDMS chains – as evidenced by the comparatively small increase in τ as a function of co-*m*CB level.

Normal-mode motions of extended *co-mCB* segments. A 3rd distinct relaxation was observed in the PDMS/PDMS-*co-mCB* hybrid systems over a temperature range of 35-80 °C. The data for this relaxation process at 50°C is given in **Figure 6**.

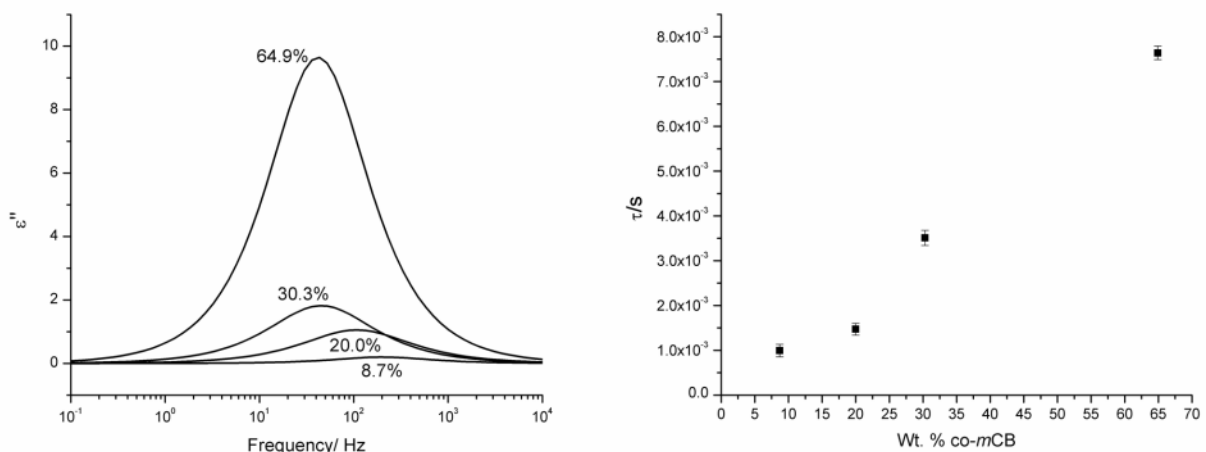


Figure 6. *Left:* An observed high temperature relaxation at 50°C as a function of wt. % *co-mCB* in the hybrid PDMS elastomers - attributed to a large-scale cooperative *normal-mode* motion of the PDMS-*co-mCB* chains. *Right:* the relaxation time for the normal motion at 50 °C as a function of *co-mCB* incorporation level. With increasing *co-mCB* content, τ is observed once again to increase.

The relaxation observed in the PDMS-*co-mCB* systems at above ambient temperatures has been attributed to a large scale cooperative ‘normal-Mode’ motion of the PDMS-Carborane copolymer segments. Such higher order cooperative relaxation behavior can be observed in polymeric systems above their T_g when both the directional and electric vectors of the chain dipoles are identical; the resultant motion of the polymer is therefore a cooperative global movement described in terms of a normal-mode of motion. Normal-mode relaxations are potentially interesting as they can yield information over a size scale greater than that of the α -segmental motions and have been observed in both PDMS melts [31] and filled elastomeric networks [20] however this is the first instance in which a normal mode motion has been observed in hybrid elastomer system such as PDMS/PDMS-*co-mCB*. As such, both the assignment and order of this observed process is the subject on ongoing investigation by means of 2D correlation nuclear magnetic resonance (NMR) studies.

The data given in **Figure 6** clearly shows that the amplitude of normal-mode response follows a non-linear relationship with the level of *co-mCB* incorporation, and the strength of this relaxation process increases exponentially as a function of *mCB* content. Additionally, this process is sensitive to the global reduction in mobility and stiffening of the network and τ is observed to increase as a function of *mCB* inclusion level within the network. Indeed, it appears that this higher order process is similar in sensitivity to changes in the motional environment as the PDMS segmental α -relaxation. Of all the relaxations observed in this study, the *co-mCB* normal mode process is the only one which obeys an Arrhenius temperature dependence. This relationship is shown for each PDMS/PDMS-*co-mCB* system in **Figure 7**. Calculated apparent activation energies and pre-factors for each relaxation are given in **Table 2**.

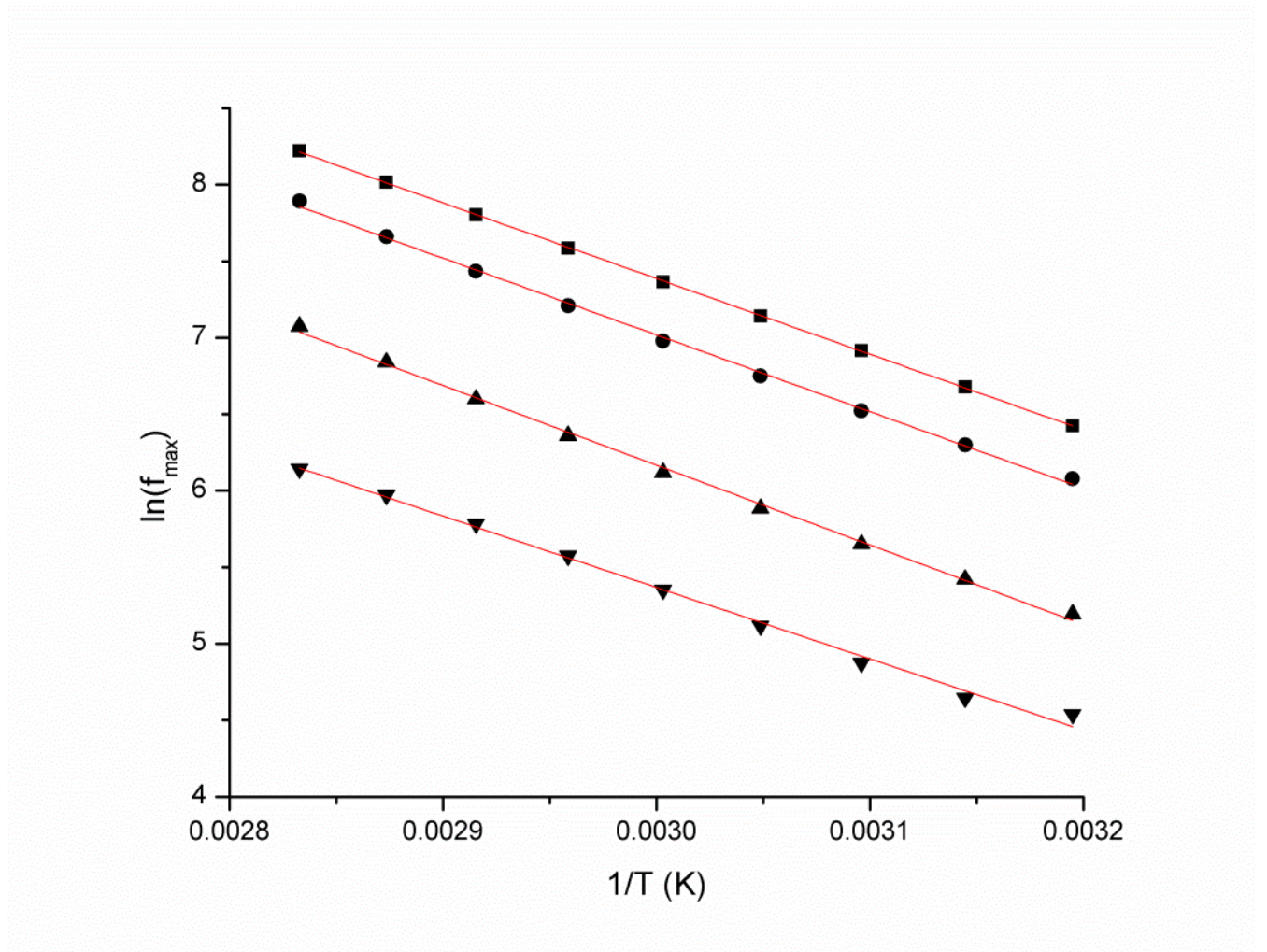


Figure 7. Arrhenius plots for the observed normal-mode relaxations of the PDMS/PDMS-*co-mCB* elastomer systems. Square, circle up-triangle and down triangle symbols correspond to the 8.7, 20.0,

30.1 and 64.9 wt. % co-*m*CB systems respectively. The straight lines correspond to linear fits of each data set from which apparent activation energies and pre-factors have been determined (see **Table 2**)

wt % co- <i>m</i> CB	Prefactor /s ⁻¹	Apparent E _A /kJmol ⁻¹
8.7	22.22 ± 0.22	41.11 ± 0.62
20.0	22.07 ± 0.22	41.72 ± 0.58
30.3	21.79 ± 0.25	43.31 ± 0.70
64.9	19.96 ± 0.18	40.49 ± 0.72

Table 1. Calculated Arrhenius pre-factors and apparent activation energies for the observed normal-mode relaxations of the PDMS-co-*m*CB chain segments. Note that while the collisional pre-factor decreases as a function of co-*m*CB inclusion level, the apparent activation energy for the motional process does not change significantly.

The fact that the observed normal mode motions of extended PDMS/co-*m*CB chains within the hybrid elastomer systems follow a simple Arrhenius temperature dependence is perhaps less surprising than the fact that the apparent activation energy for this chain motion is insensitive to co-*m*CB level and the associated reductions in global network mobility. We do however observe a very real decrease in the collisional pre-factor as a function of increasing wt. % co-*m*CB and may interpret the kinetic data therefore as simply demonstrating that while the frequency of large chain motions is depressed significantly in the PDMS/co-*m*CB systems, the energetic favorability of the normal mode-motion has not detectably decreased.

CONCLUSIONS

In this study we have demonstrated that the inclusion of a PDMS-co-*m*CB copolymer into a siloxane elastomer network has a significant and global impact on the motional dynamics of the network over a broad range of size and timescales. The manner in which the PDMS/*m*CB copolymer alters the dynamics of the PDMS network is both significantly more profound and predictable than the effects of a conventional heterogeneous boron nitride ‘filler’ phase on PDMS. Dielectric relaxometry analysis has shown that the primary segmental alpha relaxation of the PDMS chains is significantly reduced by the presence of PDMS/co-*m*CB segments within the networks whereas BN induces plasticization at high

loadings. We have also observed higher order cooperative (normal-mode) motions of extended segments of the Carborane-siloxane co-polymer chains at elevated temperatures. These normal mode motions have been shown to follow an Arrhenius temperature dependence and while they sensitive to their local chemical environment in a time domain, the energetic favorability of these large-scale relaxation processes is unaffected by the global changes to the network motional environment.

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